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Lead and Mercury Distribution in the Peat Deposits of West Siberia (Vasyuganye Peat Bogs)

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Abstract

Results are presented concerning the determination of lead and mercury total content in oligotrophic peat bog deposits in West Siberia. It is demonstrated that the current level of atmospheric lead fall-out is insignificant, the lead concentration in the upper layers of peat deposits are far below the level of background values established for other territories. Data concerning the mercury concentrations are comparable with those obtained earlier for other background areas. The distribution of elements depending on the physical and chemical properties of peat was revealed. A selective absorption of heavy metals by the humic and fulvic acids of peat organic matter was found to occur.

Key words: lead, mercury, peat deposits, West Siberia

INTRODUCTION

In recent years, especially urgent is to study natural components those can serve as indicators of the atmospheric emissions of heavy metals. In this regard, of certain interest are peat bogs. Being autonomous geochemical complexes, these systems are dependent on supplying substances from atmospheric channels and are characterized by a relatively homogeneous structure of vertical profile. Owing to this, they could be used as natural indicators of elemental flows in an historical shear [1-3,5]. In the course of studying the global and regional transport of scattered elements and their compounds, particular attention is paid to the elements those are of ecotoxicological interest, such as lead [1-6] and mercury [5-13].

Unlike other natural formations, peat bogs are characterized by an extremely high content of organic matter, namely of the two main series such as humic acids (HA) and fulvic acids (FA). Forming strong organo-mineral complexes they cause increasing the mobility and

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concentrating ability for many metals, including toxic ones, which could result in changing the dynamics of many biogeochemical processes, as well as in the formation of entire geochemical provinces with a high content of toxic elements [14]. As far as the lead and mercury are concerned, the mentioned aspect is important therewith, because among the elements most dangerous and toxic with respect to the environment and humans these elements occupy one of the first places to acquire the status of global pollutants for the last decade.

Currently, the West Siberia represents a region with intensive development of extractive industries (oil, gas, ore, and timber). Accounting for the incoming, migration and accumulation of heavy metals in peat deposits is required for deciding many issues those arise during the development of wetlands. In this regard, of paramount importance for the West Siberia, as a region with a heightened sensibility to human-caused impact, is an environmental function of peat lands those play a role of naturally occurring filters. The aim of the present work consisted in assessing and revealing the distribution of lead and mercury over the oligotrophic peat deposits of the West Siberia.

EXPERIMENTAL

The distribution of lead and mercury was studied in three polygenetic cuts across three biogeocenoses with the following landscape profile: open sedge-sphagnum bogs (OSSB), pineshrub-sphagnum phytocenosis in low and high ryams (raised bogs) (LR and HR, respectively). The landscape profile is located at the northeastern branches of the Great Vasyugan Bog (Tomsk Region, Bakcharskiy marsh district, the permanent establishment "Vasyuganye" attached to the IMCES of the SB RAS, SibSRIAP of the SB RAAS, Tomsk).

Data concerning the thickness, structure and physicochemical properties of peat deposits are

presented in Table 1. In order to perform chemical analysis, of the samples peat were taken from each genetic horizon of the peat deposit occupying a certain biogeocenosis, with the use of a TBG-1 peat bore. The determination of total lead content was performed by means of atomic emission spectral analysis using a STE-1 quartz spectrograph at the Laboratory of Mineralogy and Geochemistry of the Tomsk State University according to a certified technique described in [15]. The detection limit was equal to 0.1 mg/kg, the determination error being less than 25 %. The mercury content was measured using a RGA-11 mercury analyzer by means of atomic absorption spectroscopy. The detection limit was 0.1 ng/g; the determination accuracy was equal to 30 % [16]. The accuracy and the correctness of the results were checked using the State Standard reference samples with certified mass fractions of the elements: those based on unconsolidated

TABLE 1

Lead and mercury concentration (mean value±standard deviation, for the solid dry matter) and physicochemical properties of peat species in peat deposits

Layers, cm	Peat species and type	R, %	A, %	pН	Content				
					Pb, mg/kg	Hg, $\mu g/kg$			
0-50	Sphagnum-hollow, H	10 - 15	3.00	2.9	3.20 ± 0.25	82.9 ± 23.9			
50 - 100	The same	20	2.97	3.4	1.55 ± 0.07	53.1 ± 4.9			
100-150	Sedge and sphagnum, I	35	4.82	3.9	0.92 ± 0.03	56.4 ± 6.2			
150 - 200	Sedge, I	50 - 55	6.10	4.2	0.57 ± 0.02	22.4 ± 2.6			
200 - 250	Grass, V	50	6.36	4.5	0.27 ± 0.02	19.3 ± 0.5			
250 - 270	Fern, V	50 - 55	10.40	4.5	1.08 ± 0.03	32.5 ± 7.3			
Pine-shrub-sphagnum phytocenosis (low ryam)									
0-50	Fuscum, H	0 - 5	3.15	2.6	3.80 ± 0.10	80.7 ± 21.9			
50 - 75	The same	0 - 5	2.08	2.5	1.38 ± 0.06	62.7 ± 13.2			
75-100	Medium, H	0 - 5	2.14	2.6	1.06 ± 0.01	43.4 ± 18.2			
100-150	The same	10	4.69	3.0	0.98 ± 0.03	38.1 ± 7.7			
150 - 200	Pine-cotton grass, I	50 - 55	5.89	3.5	0.75 ± 0.03	44.9 ± 13.1			
200 - 250	Sedge, V	50 - 55	6.53	4.2	0.38 ± 0.04	26.8 ± 0.4			
250-300	Grass, V	40 - 45	6.30	4.4	1.38 ± 0.02	23.9 ± 3.65			
Pine-shrub-sphagnum phytocenosis (high ryam)									
0-25	Pine-cotton grass, H	45 - 50	5.50	3.6	4.50 ± 1.11	137.4 ± 42.4			
25 - 50	Wood-cotton grass, I	45 - 50	7.73	4.5	2.28 ± 0.14	119.3 ± 12.3			
50 - 75	The same	55 - 60	9.02	5.0	1.14 ± 0.07	100.7 ± 14.5			
75-100	The same	55 - 60	9.42	5.1	1.28 ± 0.04	77.5 ± 7.9			

Note. R is the decomposition level of peat; A – ash; H – high-moor, I – intermediate, V– valley peat types, respectively.

carbonate-silicate sediments (SGHM-1, SGHM-3) and on aluminosilicate sediments (SGHM-2, SGHM-4) as well as standard reference samples of the aqueous solutions of mercury ions (GSORM 1).

The botanical composition and the decomposition level of peat were determined by means of a technique described in [17], the ash level was fixed according to [18], the exchange acidity was determined as reported in [19]. The fractional group composition of organic matter was determined by means of the method described in [20] at the Laboratory of Peat and Ecology of the Siberian Research Institute for Agriculture and Peat of the SB RAAS (Tomsk Region) [21]. The absolute age of peat samples was determined by means of radiocarbon dating at the Laboratory of Cenozoic Geology and Paleoclimatology of the Institute of Geology and Mineralogy of the SB RAS (Novosibirsk).

RESULTS AND DISCUSSION

The minimum concentration of lead in peat deposits inherent in OSSB and LR are attached to a layer occurring at a depth of 200-250 cm, whereas that in peat deposits inherent in HR are attached to a layer occurring at a depth ranging within 50-75 cm, *i. e.*, to the layers of peat, formed no later than the 2-2.5 thousand years ago (see Table 1). Above this depth the lead concentration begins gradually increasing. The overall paleogeographic situation in the forest zone of the West Siberia at that time allows one to suggest that the main source of lead in the upland bogs consisted in the vegetation of the areas surrounding the bogs. A similar pattern is observed for mercury: minimum mercury concentration values are observed within the near-bottom layer and the layer thereover. Low concentration level of the elements at the bottom part of peat sections indicates a low content of these elements in the atmosphere at the time when these layers were located on the surface.

The maximum Pb and Hg concentration values are registered in the upper (0-50 cm) layer of peat profiles in the case of OSSB and LR and at a depth of 0-25 cm – in the layer of HR peat sections. Increasing the concentration

of Hg and Pb in the peat bogs from the bottom layers to the surface is a common feature of peat bogs which indicates an increase in atmospheric emissions during the last millennium [1-3, 5, 9].

At the same time, the maximum lead concentration values obtained (3.2-4.5 mg/kg)are comparable with those inherent in wetlands of Eurasian background territories (4.0 mg/kg) [22] and the bogs of the West Siberia: 3.1 and 4.8 mg/kg for the Tomsk [23] and the Tyumen [24] Regions, respectively. (It should be noted that the latter were obtained by means of averaging the entire profile of peat.) Generally, the results obtained are in a satisfactory agreement with the mean value reported for peat species inherent in the European Territory of Russia (3.0 mg/kg [25]), but the values are smaller as to compare with the data for the peat bogs of the Russian plain (the average value for the layer 0-50 cm thick is equal to 9.9 mg/kg [1]). Our data concerning the content of lead are also substantially lower in value than the data reported for the Northern Europe. Thus, the native peat bogs of Finland at a depth of 0-40 cm layer exhibit the lead concentration equal to 11.3 mg/kg, whereas for the layer at a depth of 40-80 cm the value is equal to 5.3 mg/kg [26]. The background concentrations of lead (3.8-8.3 mg/kg) for the wetlands of Finland [27] are similar in the value with respect to our data, but these values were obtained for the depth ranging from 4.0 to 6.7 m. The maximum concentration of Pb (80 mg/kg [3]) was reported for the bogs of Switzerland (Jura Mountains).

The data obtained concerning the mercury are similar to the data reported both for the depth profiles of Patagonian bogs, and for Antarctic ice [10]. For the upper layers of OSSB and LR peat deposits, the mercury concentrations is to a considerable extent lower than those for the peat bogs of the Northern Sweden (the average value being equal to 198.3 ng/g within the layer ranging from 11 to 16 cm [12]). The concentration of Hg in organic soils of Canada varies within the range from 120 to 300 ng/g [11]. The maximum concentration values obtained for mercury inherent in Sweden peat bogs Dumme Mosse and Trollsmosse (from 130 to 460 μ g/kg [5]), are also much higher as to compare with our data. Comparable with our results of determining the concentration of mercury in peat bogs of the northeastern China are also comparable with the data we obtained (the average value for the layer of 5-55 cm is equal to 106.6 ng/g [13]).

On the basis of determining the absolute age it was found that the upper layers of peat enriched with mercury and lead to a greatest extent, were formed within the last 550-850 years. These results are in a good agreement with the data for the moderate climatic zone of the West Siberia [24]. It should be noted that the increase in atmospheric deposition of metals (Pb, Cu, Fe) in this region occurred much later (600-700 years ago) as to compare with the territories of the European part of Russia, where the impact of man-caused sources on lead intake was observed for the layers of peat bogs dated to 1.5-2.0 thousand years. To all appearance, the process of atmospheric dusting in the territory of the West Siberia could be connected with agricultural expansion accompanied by burning the forests. (Widespread farming began in this region with the arrival of Russian population, about 450 years ago [24].)

Thus, data concerning the content of Pb and Hg in the peat deposits within the background areas remote from any contamination sources indicate that the current level inherent in atmospheric deposition of these elements is negligible. The materials obtained support the possibility of using the marsh landscapes as natural plan-tables in the course of studying of heavy metal polluted areas, and oligotrophic bogs are most suitable for these purposes.

The distribution of mercury and lead in the thick peat deposits is similar in nature, *i. e.*, the accumulation of these elements occurs in parallel, except for bottom layers, wherein the concentration of lead slightly increases, where-

as as far as mercury is concerned, the concentration, on the contrary, decreases, reaching a background level inherent in the bedrock of West Siberia (see Table 1). Increasing the concentration of lead within the bottom layers of peat deposits could be caused by supplying it from soil-forming rocks. The coefficients of determination between these elements within the interior of peat deposits are quite high (for OSSB $R^2 = 0.85$, for LR $R^2 = 0.53$ for HR $R^2 =$ 0.88), which indicates that there occurs a similar orientation in the geochemical migration of these elements in the course of peat genesis. According to the geochemical classification by Goldschmidt [28], these elements according to their physicochemical properties and the affinity to sulphur are considered to belong to the group of chalcophilic elements.

The distribution of lead and mercury in the vertical profile of the peat layer is characterized by a pronounced negative correlation with ash content, the decomposition level, and pH (Table 2). A certain role in the distribution of elements is played by a horizontal flowage of a bog tract, determined by a slope of groundwater free surface. For example, data concerning the concentration of Hg in peat deposits of the terrain profile indicate the fact that there is an increase in the concentration observed along the seepage from OSSB to HR. The concentration of mercury in the peat deposits of HR is 1.5-2 times higher than that observed for peat deposits inherent in LR and OSSB. Thus, the peat deposit inherent in HR on the terrain profile under consideration serves as a geochemical barrier with respect to mercury. On the contrary, the behaviour of lead in the landscape is more stable, the values of its content in the peat deposits of OSSB, LR, HR are comparable, which is in a good agreement with the series of migration and biological mo-

TABLE 2

Lead and mercury distribution in the peat deposits under investigation depending on peat physicochemical properties

Parameters	Lead			Mercury	Mercury		
	OSSB	LR	HR	OSSB	LR	HR	
Ash content, %	-0.46	-0.36	-0.96	-0.61	-0.84	-0.99	
Decomposition level, $\%$	-0.79	-0.46	-0.92	-0.84	-0.56	-0.74	
pН	-0.90	-0.62	-0.98	-0.88	-0.80	-0.71	

bility of the element, wherein it occupies one of the last places [14].

The migratory ability of metals in marsh landscapes is controlled primarily by the composition of humic acids as well as competitive complex formation between the elements and humic (HA) and fulvic acids (FA) [14]. If the interaction with FA results in an abrupt increase in the scattering of HM, the reactions of HM ions with HA as the most poorly water-soluble and high molecular group of humus acids gives an opposite geochemical result. Humic acids behave as complex-forming sorbents those provide concentrating the HM in the environment.

The correlation coefficients we obtained for the distribution of mercury and lead indicate the fact that there is connection between the elements and the features of the fractional composition of peat organic matter (Fig. 1). There was a negative correlation revealed concerning the distribution of the elements for HA and positive one for FC, which could be connected with a specific chemical nature of different fractions of humus substances (HA1, HA3), as well as with the laws of their distribution within the profile of peat deposits caused by oxidation-reduction processes. Under an aerobic conditions inherent in lower peat deposit horizons the HA content for all the fractions exhibits an increase. Fulvic acids represent more oxygenated compounds as to compare with HA being more inherent in the surface horizons of peat deposits.

It is considered that among all of the divalent ions the mercury exhibits the highest affinity with respect to organic humus substances [14]. A high positive correlation between mercury and organic carbon was observed for bottom sediments and suspended matter of water reservoirs [29, 30], peat bogs [6, 7].

Mercury takes first place among the heavy metals according to the stability of fulvic and humate complexes. Data available from the literature [29] concerning the sorption of Hg(II) on HA demonstrate so high stability of these compounds that in the precipitation of humates



Fig. 1. Correlation between distribution of Pb and Hg with the content of different fractions of organic matter in OSSB peat deposits (a), LR (b) and HR (c) peat deposits on the landscape profile.

the mercury cannot be substituted even by the ions of trivalent and tetravalent elements. The sorption capacity of the HA with respect to Hg(II) ions reaches the values of 340 mg/g or 3.4 mg-eq/g even at pH 3.0, whereas 1 g of HA within the range of pH 5.0-6.0 can absorb 34.0 mg Pb(II) [31]. At the same time it is proved that the sorption of mercury on HA occurs according to a complex formation mechanism.

The correlation analysis performed has demonstrated that the distribution of Hg in peat deposits is to a greater extent dependent on the distribution of all the factions of the HA. For the peat deposits of OSSB, a positive correlation is revealed between the content of mercury and the content of FA (fraction 3). The character of lead distribution is to a lesser extent affected by humic substances. There was a negative correlation revealed between the distribution of lead and the content of HA (fraction 3), at the same time the correlation parameters vary within a wide range. The correlation pronounced to a maximum extent is observed for OSSB and HR peat deposits.

CONCLUSION

1. The materials obtained concerning the content and features of Pb and Hg distribution in peat deposits support the possibility of using wetland ecosystems as natural indicators in the course of retrospective studies on heavy metal polluting the vast territories of Siberia. The present level of Pb and Hg atmospheric deposition in the territory under investigation is insignificant, whereas their maximum content in peat sections correspond to the level of background areas.

2. Pb and Hg distribution in thick peat deposits is revealed depending on the physicochemical properties of peat such as decomposition level, ash content, pH.

3. A selective character is established for the interaction of different fractions of peat organic matter with Pb and Hg concentration. The distribution of Hg in peat deposits is to a greater extent dependent on the distribution of all the factions of HA. On the contrary, humic substances do not play such an important role in the distribution of Pb; a negative correlation with the distribution of Pb is revealed only for HA fraction 3.

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